STEEL
Success Story

Recovering Acid and Metal Salts from Pickling Liquors

Acid and Salt Recovery Now Cost-Effective at Point of Use

Benefits

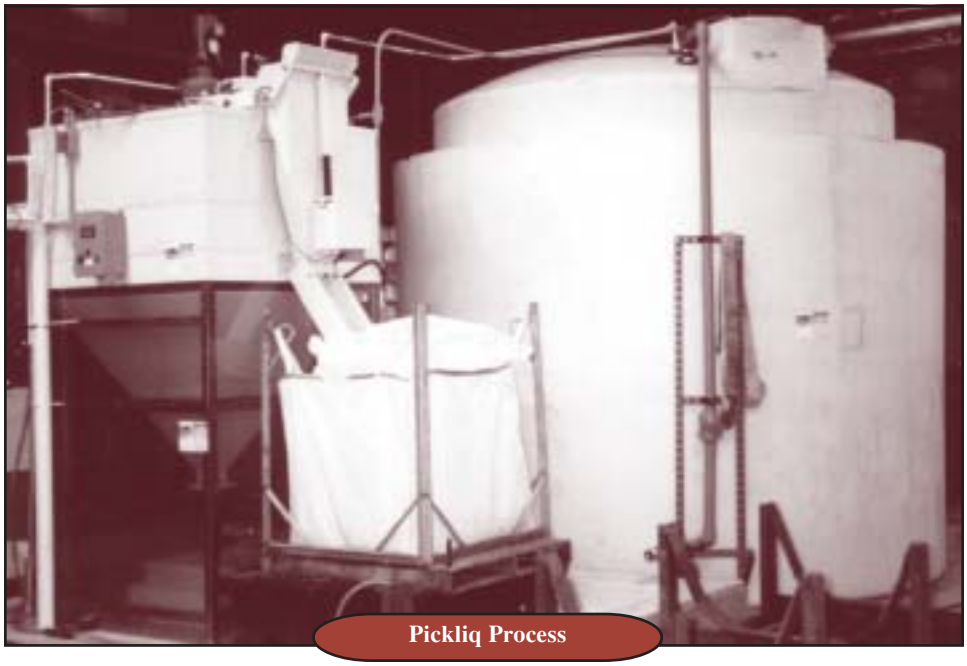
- Recycles acid for reuse, eliminating transportation and disposal of spent acid and neutralized sludge
- Has provided cumulative energy savings of 5.8 billion Btu through 2000
- Generates saleable metal salts that can be used in various applications
- Has avoided 390 tons of CO_2 emissions from fuel combustion through 2000
- Reduces the demand for virgin acids, conserving petroleum feedstock
- Has saved $74,000 in avoided fuel purchases through 2000

Applications

The Pickliq process has widespread application in the primary metals industry for recovering waste pickling liquor at the point of use. The process is also applicable in the metal-finishing and circuit board industries for recovering acids and metal salts from all types of etching and metal stripping.

Metal fabrication processes often use pickling baths (immersing metal in an acid) to clean and remove oxide layers from metal. When its acid strength is depleted, the pickling bath is replaced with a new bath of fresh acid and other components. The used or waste pickling bath is then neutralized with caustic soda and transported in tank trucks to a regeneration facility or disposal site. Offsite waste treatment and disposal of the waste pickling bath are very expensive.

The Green Technology Group, Inc., invented the Pickliq® process for recycling sulfuric acid from waste pickling liquor at the point of use. Two full-scale systems currently are in operation on steel pickling lines operated by O. W. Hubbell & Sons, Inc. (New York Mills, New York) and PTC Alliance, formerly Pittsburgh Tube Corporation (Monroe, New York).



Pickliq Process

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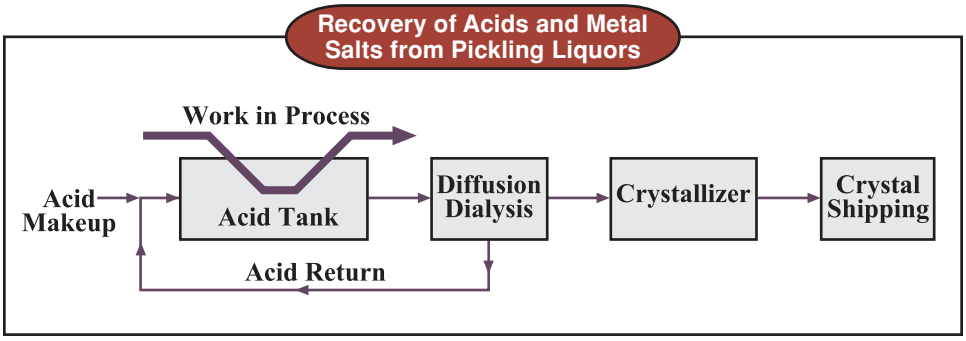
In collaboration with the U.S. Department of Energy's Inventions and Innovation Program, Green Technology Group conducted pilot studies for recycling sulfuric acid and hydrogen peroxide solutions from etching copper. The grant established that the Pickliq process can be successfully applied to recovering these solutions for cleaning both ferrous and nonferrous metals.

Green Technology Group conducted the pilot-scale studies at Phelps Dodge Copper Products Company's pickling operations in El Paso, Texas. The pilot studies were extremely useful in identifying the special requirements for applying the Pickliq process to the copper rod and wire industry. Sulfuric acid, hydrogen peroxide, and copper sulfate pentahydrate salt crystals were successfully recovered. The grant's activities also included testing the Pickliq process for recovering hydrochloric acid from steel pickling plants, but tests indicated that process modifications were needed. These modifications were later developed and are being tested with support from DOE's NICE[3] (National Industrial Competitiveness through Energy, Environment, and Economics) Program. The tests will be completed in January 2002.

Technology Description

The Pickliq technology is a novel combination of membrane diffusion dialysis and low-temperature crystallization. As the figure shows, a side stream of depleted acid is taken from the pickling tank and passes through the diffusion dialysis membrane. The purified acid product is returned to the pickling tank while solution containing metal salt is sent to the low-temperature crystallizer. The salt is crystallized, and the crystallizer dewaters the crystals in a centrifuge and drops them into bulk shipping containers. Throughout this process, specially designed heat exchangers cool the incoming waste acid using the low-temperature effluent from the crystallizer. Interchanging heat from these streams saves up to 50% of the power required for the crystallizer.



Capabilities

- Permits continuous operation of the pickling bath while maintaining the acid bath at optimum concentration
- Significantly improves pickling process uniformity and product quality and reduces downtime and rework
- Significantly increases productivity in pickling operations and minimizes waste

"Results of the I&I grant established performance parameters for the Pickliq process."

– Douglas Olsen
President
Green Technology Group, Inc.

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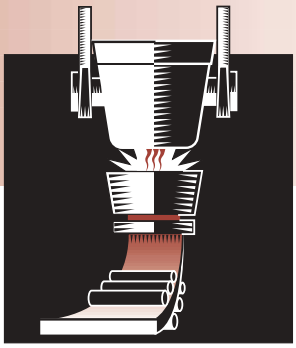

Project Partners
- Inventions and Innovation Program
  Washington, D.C.
- Green Technology Group, Inc.
  Pawling, NY
- Phelps Dodge Copper Products Company
  El Paso, TX
- O. W. Hubbell & Sons, Inc.
  New York Mills, NY
- PtC Alliance (formerly Pittsburgh Tube Corporation)
  Monroe, NY

Energy Savings and Pollution Prevention

Besides saving energy, the Pickliq process makes onsite sulfuric acid recovery cost effective for steel pickling baths. Its implementation allowed O. W. Hubbell & Sons to incorporate pollution prevention measures into their daily operations. PTC Alliance is significantly reducing the acid procurement and hazardous waste disposal costs of its steel tubing operations.

The table below shows the life-cycle energy requirements for 1 ton of sulfuric acid. Therefore, each ton of sulfuric acid recycled will save~10 million Btu. The expected benefit has been applied to the two operating facilities that together process about 2,300 tons per year of waste acid. This acid exits from pickling operations at about 6 weight percent, which represents about 140 tons of recycled sulfuric acid on a 100% basis. At 10 million Btu per ton, the annual energy savings are about 1.38 billion Btu. Cumulative energy savings though 2000 total 5.8 billion Btu since 1995. Cumulative savings from avoided energy purchases through 2000 total $74,000 using inflation-adjusted 1999 dollars. The associated cumulative reduction in CO_2 emissions through 2000 is 390 tons.

Estimated Life-Cycle Energy Requirements (Million Btu Per Ton of Sulfuric Acid)

Activity	Energy Use
Mining and manufacture	0.8
Delivery to plant (300 miles)	0.8
Waste return shipping	4
Lime neutralization	5
Total	~10

Source: D.R. Olsen. 1997. *Pilot Test of Pickliq Process to Determine Energy and Environmental Benefits and Economic Feasibility.* DOE/EE/15657-T1.

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Commercialization Success and Market Potential

The table below shows a hypothetical payback period of 6 months for a Pickliq system processing 5,000 gallons per day of spent copper etch solution. The actual payback period could be longer depending on sales income.

Expected Payback Period for Copper Rod Mill

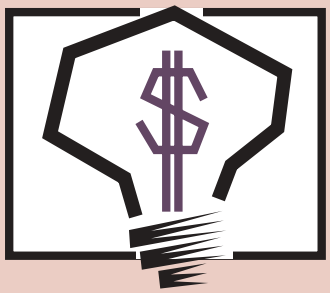
Item	Savings
Sulfuric Acid	$50,000
Hydrogen Peroxide	$500,000
Inhibitor	$100,000
Waste Treatment	$200,000
Operating Costs Savings from 3% Reject Improvement	$600,000
Sales Income (Copper Sulfate Pentahydrate)	$3,000,000
Subtotal Revenues (A)	$4,450,000
Operating Costs for Pickliq	($300,000)
Plant Cost	($2,000,000)
Subtotal Investment (B)	($2,300,000)
Simple Payback - Months (12 x B/A)	6 months

The Pickliq process has widespread application in the primary metals industry for pickling operations. It is also applicable to the metal-finishing industry for metal cleaning and the circuit board industry for recovery of acid and metal salts from all types of etching and metal stripping. Acids that can be recovered include hydrochloric, sulfuric, nitric, hydrofluoric, and others (including nonmineral acids). Metals with recoverable salts include ferrous, nickel, copper, zinc, tin, manganese, and aluminum.

Industry of the Future — Steel

Through the Office of industrial Technologies (OIT) Industries of the Future initiative, the Steel Association, on behalf of the steel industry, has partnered with the U.S. Department of Energy (DOE) to spur technological innovations that will reduce energy consumption, pollution, and production costs. In March 1996, the industry outlined its vision for maintaining and building its competitive position in the world market in the document, ***The Re-emergent Steel Industry: Industry/ Government Partnerships for the Future.***

OIT Steel Industry Team Leader: Isaac Chan (202) 586-4981.



The Inventions and Innovation Program works with inventors of energy-related technologies to establish technical performance and to conduct early development. Ideas that have significant energy-savings impact and market potential are chosen for financial assistance through a competitive solicitation process. Technical guidance and commercialization support are also extended to successful applicants.

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